(12) EUROPEAN PATENT APPLICATION

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(54) Low temperature process for depositing oxide layers by photochemical vapor deposition.

(57) The specification discloses a low temperature process for depositing oxide layers on a substrate by photochemical vapor deposition, by exposing the substrate to a selected vapor phase reactant in the presence of photo-chemically generated neutral (un-ionized) oxygen atoms. The oxygen atoms react with the vapor phase reactant to form the desired oxide, which deposits as a layer on the substrate. The use of photochemically generated neutral oxygen atoms avoids damage to the substrate due to charge bombardment or radiation bombardment of the substrate. The deposited oxide layer may optionally incorporate a selected dopant material in order to modify the physical, electrical, or optical characteristics of the oxide layer.

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LOW TEMPERATURE PROCESS FOR DEPOSITING OXIDE LAYERS BY PHOTOCHEMICAL VAPOR DEPOSITION

TECHNICAL FIELD

1   This invention relates generally to the manufacture of semiconductor devices and, more particularly, to a photochemical vapor deposition process for forming a

5   dielectric oxide layer on the surface of a selected semiconductor material or an optical substrate, using a low temperature and non-ionizing radiation.

BACKGROUND ART

10   In the manufacture of semiconductor devices, it is frequently necessary to form a dielectric layer either as a passivation layer to permanently protect the surface of the substrate or as a mask during such procedures as etching, solid state diffusion, or ion-implantation.

15   One method by which an oxide layer, such as silicon dioxide (SiO_2), may be formed is a plasma-enhanced chemical vapor deposition process as described by James A. Amick, G. L. Schnable, and J. L. Vossen, in the publication entitled, "Deposition Techniques for

20   Dielectric Films or Semiconductor Devices," in the Journal of Vacuum Science Technology, Vol. 14, No. 5, Sept.-Oct. 1977, pp. 1053-1063. In such a plasma-enhanced process, the vapor phase reactants, such as silane (SiH_4) and nitrous oxide (N_2O), are subjected

25   to a radio frequency discharge, which creates an ionized plasma of the reactant gases. These ionized reactants then interact to form the desired reaction

1   product. However, as a result of the exposure of the
reactant gases to the radio frequency discharge, numerous
extraneous ionized and neutral particles, as well as high
energy radiation with wavelengths as low as 500 angstroms
5   (Å) and even extending into the x-ray region, are pro-
duced and bombard the surface of the substrate on which
the oxide is being formed. If the substrate comprises
a sensitive device type, such as a charge coupled device
or a device formed of certain compound semiconductors
10   (e.g., InSb, HgCdTe, or GaAs), the above-described charged
particles and unwanted radiation frequently impart damage
to these sensitive devices. For example, the deposited
oxide layer may incorporate charges or dangling bonds,
which create high surface state densities ($\mathcal{N}_{ss}$) at the
15   semiconductor device/oxide layer interface and which
will trap charges when a voltage is applied to the device,
thereby preventing optimum device performance. In
addition, a plasma enhanced deposition process has the
disadvantage that plasma-induced heating of the substrate
20   occurs as a result of selective absorption of the radio
frequency energy by the substrate, and this heating causes
uncertainty in the temperature of the substrate, which
prevents optimization of the characteristics of the
deposited oxide layer.

25   Other methods by which oxide layers may be formed
use a non-reactive or a reactive sputtering technique.
By a non-reactive sputtering technique, as described,
for example, by Amick et al as referenced above, a disk
of the selected oxide material, such as SiO_2, is bom-
30   barded with argon ions, which cause the SiO_2 to vaporize,
and the vaporized SiO_2 subsequently deposits on the selec-
ted substrate. By a reactive sputtering technique, as
described, for example, by Amick et al as referenced above,
a disk of silicon is bombarded with oxygen ions, which
35   causes vaporization of the silicon, and the vaporized
silicon and oxygen ions then react to produce the desired

1   SiO_2. However, these sputtering techniques are similar
to the above-described plasma processes in that they fre-
quently impart damage to sensitive devices due to charge
bombardment or radiation bombardment of the device. In
5   addition, the films produced by sputtering techniques
are often granular, not dense, and not specular (i.e.,
having good light reflecting properties).

Both the sputtering technique and the plasma-
enhanced method for chemical vapor deposition may be
10   used to deposit a dielectric layer which incorporates
a selected dopant material. In the former case, an
appropriately doped target could be bombarded by
selected ions. In the latter case, a dopant-containing
material is added to the reactant gases which are then
15   ionized. However, both the above sputtering technique
and the above plasma-enhanced method suffer from the
difficulties discussed above, particularly that of
imparting damage due to charge bombardment or radiation
bombardment and plasma-induced heating of the substrate.
20   Still another method by which oxide layers may be
formed involves thermal processes as described by
Amick et al as referenced above. In order to form SiO_2,
for example, by a thermal process, silane is brought
into contact with oxygen at a low temperature and a
25   spontaneous reaction occurs, forming SiO_2. The films
formed by thermal processes, however, are usually granu-
lar, do not necessarily have good adhesion, and tend
to incorporate traps.

It is the alleviation of the prior art problem
30   of imparting damage to sensitive devices due to charge
bombardment or radiation bombardment during the formation
of an oxide layer thereon to which the present invention
is directed.

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BAD ORIGINAL

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SUMMARY OF THE INVENTION

The general purpose of this invention is to provide
a new and improved process for depositing a layer of an
oxide of a chosen material on the surface of a selected
5 substrate by low-temperature photochemical vapor depo-
sition. This process possesses most, if not all, of the
advantages of the above prior art oxide deposition pro-
cesses, while overcoming their above-mentioned significant
disadvantages.
10 The above general purpose of this invention is
accomplished by exposing the substrate to a selected
vapor phase reactant in the presence of photochemically
generated, neutral (unionized) oxygen atoms. The oxygen
atoms react with the vapor phase reactant to form the
15 desired oxide, which deposits as a layer on the substrate.
The use of photochemically generated neutral oxygen atoms
avoids damage to the substrate due to charge bombardment
or radiation bombardment.

Accordingly, it is an object of the present
20 invention to provide a new and improved process for
depositing a layer of an oxide of a chosen material on
the surface of a selected substrate by a novel, low-
temperature chemical vapor deposition process which avoids
damage to the substrate from charge- or radiation-
25 bombardment.

Another object of the present invention is to pro-
vide a process of the type described which minimizes the
value of the surface state density at the oxide/semicon-
ductor substrate interface and thus minimizes the charge
30 traps in the deposited oxide layer.

Still another object is to provide a process of
the type described which produces a low density of
generation/recombination centers in the deposited oxide
layer, and thus provides good minority carrier lifetime
35 and reduced susceptibility to radiation damage in the
device formed by this process.

5

Another object is to provide a process of the type
described which is performed at a temperature as low as
room temperature (e.g. 30°C) and thus eliminates the
problems of boundary migration and the resulting decreased
device yields which are encountered in the fabrication
of high density/high speed devices at higher temperatures.

Yet another object of the present invention is to
provide a process of the type described which produces
dense, non-granular, adherent oxide films on selected
substrates.

Another object of the present invention is to
provide a new and improved process for depositing a
layer of a chosen oxide containing a selected dopant
material on the surface of a substrate by a chemical
vapor deposition process which avoids damage to the sub-
strate due to charge bombardment or radiation bombardment.

Still another object is to provide a new and
improved process for depositing a layer of a chosen oxide
containing a selected dopant material on the surface
of a substrate, which uses a photochemical technique.

The foregoing and other objects, features, and
advantages of the present invention will be apparent
from the following more particular description of the
preferred embodiments of the invention, as illustrated
in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates, in schematic form, a preferred
apparatus for carrying out the processes according to
first and second embodiments of the present invention,
in which neutral oxygen atoms are formed by the mercury
photosensitized dissociation of an oxygen-containing
precursor and are reacted to form an undoped or a doped
oxide layer, respectively.

FIG. 2 illustrates, in schematic form, a preferred
apparatus for carrying out the processes according to

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third and fourth embodiments of the present invention,
in which neutral oxygen atoms are formed by the direct
dissociation of an oxygen-containing precursor and are
reacted to form an undoped or a doped oxide layer,
respectively.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows, in simplified form, an apparatus suitable
for implementation of two process embodiments of the present
invention in which neutral oxygen atoms are formed by the
mercury photosensitized dissociation of a chemically
unreactive oxygen-containing precursor, such as nitrous
oxide (N_2O), molecular oxygen (O_2), or nitrogen dioxide
(NO_2). (The term "chemically unreactive" is used herein
to denote that a substance will not react with the
designated reactants under normal mixture conditions.)
A reaction chamber 10, in which the chemical vapor depo-
sition reaction occurs, is provided with a quartz window
12, which is integral with the top surface of the reaction
chamber 10. The quartz window 12 is transmissive to the
selected wavelength of radiation used to initiate the
desired photochemical reaction to be discussed below,
and this radiation 14 of a selected wavelength is produced
by the radiation-producing means 16, which may be, for
example, an array of low pressure mercury vapor arc lamps.
Within the reaction chamber 10, there is a substrate
holder 18, which receives a substrate 20 onto which the
desired oxide layer is to be deposited.

External to the reaction chamber 10 and adjacent to
the bottom surface thereof, there are heating elements
21, which may be formed, for example, of Nichrome wire
and are activated by applying a controlled voltage
thereto. The heating elements 21 may be used optionally
to heat the substrate 20 to the required temperature
so that appropriate properties of the deposited layer,
such as density, may be obtained. The temperature in

1   the chamber 10 may be maintained as low as room temper-
ature (i.e. 30°C) or as high as required (e.g., 300°C
or higher). However, since mercury vapor arc lamps, for
example, become less efficient at increased temperatures,

5   it is necessary to provide external water cooling or an
external air or nitrogen cooling source to cool these
lamps and remove radiant heat produced by the substrate 20
and substrate holder 18 at certain elevated temperatures
(as high as 600°C, for example, or higher). For this

10 purpose, the radiation-producing means 16 is completely
contained within the enclosure 23, which may be formed
of aluminum, and an external cooling means 25, such as
pipes with water flowing therethrough as shown in FIG. 1
or flowing nitrogen gas, is activated to apply cooling

15 to the enclosure 23. The enclosure 23 is secured to the
outside surface of the reaction chamber 10 which surrounds
the quartz window 12, but may be removed therefrom as

required. Thus, the processing temperature is maintained
at a level such that sufficient cooling of the mercury

20 lamps can be accomplished in order to provide efficient
lamp performance. The enclosure 23 also provides eye
protection to the operator from the radiation 14. Leading
from the reaction chamber 10, there is a tube 22 which
passes through a valve 24 and then to a vacuum-producing

25 means, such as a pump, (not shown), which is used to
evacuate the chamber 10 to a sufficiently low pressure
to allow the vapor deposition reaction to occur.

External to the reaction chamber 10, there are cham-
bers 26 and 28 which contain the individual reactant gases

30 for the selected chemical vapor deposition reaction, for
example, silane and nitrous oxide. The chambers 26 and
28 are connected to control valves or flowmeters 30 and
32, respectively, which are used to control the amounts
of reactants which are introduced into a tube 34. Alter-

35 natively, for a second process embodiment of the present
invention (discussed below), there are included a third

1   chamber 27, which contains the precursor of the selected
    dopant material, such as phosphine, and a corresponding
    control valve or flowmeter 31, which controls the amount
    of dopant precursor introduced from the chamber 27 into
5   the tube 34, where it is mixed with the other reactant
   gases discussed above.

    The reactant gases flow through the tube 34 into a
    chamber 36 which contains a pool of mercury (at room
    temperature) having mercury vapor above it, at a vapor
10 pressure of 10^{-3} Torr at 30°C. The reactant gases thus
    become mixed with mercury vapor in the chamber 36 and
    this reactant gas mixture then passes through a tube 38
    and into the reaction chamber 10, where the chemical vapor
    deposition reaction may be brought about. The components
15 of the apparatus shown in FIG. 1 may be constructed of
    stainless steel or aluminum, unless otherwise specified.
    The apparatus shown in FIG. 1 may be used for either
    a low pressure continuous flow photochemical reactor
    system, in which there is a continuous influx of reactant
20 gases and removal of reaction by-products during the
    photochemical reaction process, or for a static photo-
    chemical reactor system, in which specified amounts of
    reactants are introduced into the reaction chamber, the
    flow of reactant gases is stopped, and then the photo-
25 chemical reaction process is allowed to occur.

    In practicing the present invention in accordance
    with the first embodiment thereof, which depends on the
    photochemical generation of atomic oxygen, and using the
    apparatus of FIG. 1 with only two reactant gas chambers
30 (chambers 26 and 28), a chemical vapor deposition process
    is performed as generally described by Werner Kern and
    Richard S. Rosler in the publication entitled, "Advances
    in Deposition Processes for Passivation Films", in the
    Journal of Vacuum Science Technology, Vol. 14, No. 5,
35 Sept.-Oct. 1977, pp. 1082-1099, in the discussion of
    low pressure chemical vapor deposition processes. The

1   reaction chamber 10 is evacuated by the vacuum-producing means to a predetermined pressure, for example 1 to 4 Torr. The selected vapor phase reactant, such as SiH_4, is placed in a chamber such as the chamber 26, and a chemically

5   unreactive oxygen-containing precursor, such as N_2O, is placed in a chamber such as the chamber 28. The valves 30 and 32 are set so that the reactants from the chambers 26 and 28, respectively, in a predetermined ratio and at a predetermined flow rate may pass into the tube 34 and then

10   into the chamber 36, which contains a pool of mercury. These reactant gases become mixed with mercury vapor in the chamber 36 and pass from the chamber 36 through the tube 38 into the reaction chamber 10, which is maintained at approximately room temperature (e.g. 30°C) or up to 200°C

15   or higher. The radiation-producing means 16 is activiated and produces the radiation 14 of a selected wavelength required to produce the desired photochemical reaction (e.g. $2537\mathring{A}$ to produce mercury in an excited state). The radiation 14 passes through the quartz window 12 into the

20   reaction chamber 10, where it excites the mercury (Hg) atoms in the reactant gas mixture to form mercury atoms in an excited state (Hg*) (approximately 5 electron volts above normal ground state, but unionized), as shown in Equation (1) below. The Hg* then collides with the oxygen-

25   containing precursor, such as N_2O, and causes the precursor to dissociate and produce atomic oxygen (O), as shown in Equation (2a) below.
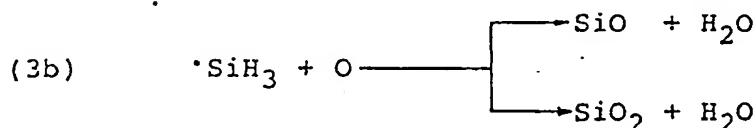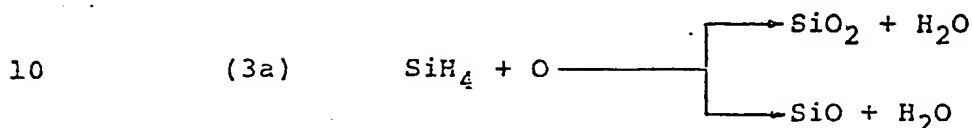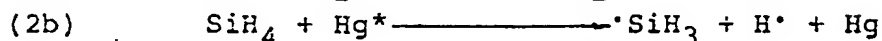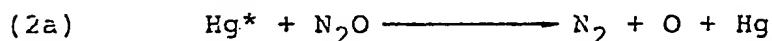
      In addition, the Hg* may react with the selected vapor phase reactant, such as SiH_4, to produce a

30   reactive radical, such as $\cdot SiH_3$, as shown in equation (2b) below. Finally, the atomic oxygen reacts with the reactant, SiH_4, or the reactive radical, such as $\cdot SiH_3$, to produce the desired oxide, such as SiO and SiO_2, as shown in Equations (3a) and (3b) below. Either SiO or

35   SiO_2 can be produced, depending on the reactant gas ratio

1   of SiH_4 and N_2O (i.e. the steady state concentration

of atomic oxygen which oxdizes SiH_4).

(1) $Hg + h\nu \ (2537\overset{\circ}{A}) \longrightarrow Hg^*$
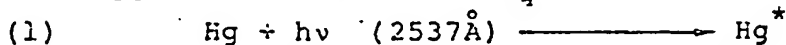
        where h = Planck's constant

5   ν = frequency of absorbed

                    radiation

(2a) $Hg^* + N_2O \longrightarrow N_2 + O + Hg$

(2b) $SiH_4 + Hg^* \longrightarrow \cdot SiH_3 + H\cdot + Hg$

10   (3a) $SiH_4 + O \longrightarrow \begin{cases} SiO_2 + H_2O \\ SiO + H_2O \end{cases}$

(3b) $\cdot SiH_3 + O \longrightarrow \begin{cases} SiO + H_2O \\ SiO_2 + H_2O \end{cases}$

15   The reaction of Hg^* with SiH_4 to form the radical

$\cdot SiH_3$ is a side reaction which is not necessary to the

process of the present invention, but leads to the same

end product as the major reaction path. The atomic oxygen

produced in Equation (2a) above may react directly with

20   the selected vapor phase reactant without first forming

an intermediate radical, as described in Equation (3a)

above.

    Alternatively, the atomic oxygen required for this

first process embodiment of the present invention may be

25   formed by the mecury sensitized dissociation of nitrogen

dioxide (NO_2) to form atomic oxygen and NO. Further,

atomic oxygen may also be formed by the mercury sensitized

dissociation of molecular oxygen in accordance with Equa-

tions (4) and (5) below, or by other known means for

30   forming atomic oxygen by photochemical processes.

(4) $Hg + h\nu (2537\overset{\circ}{A}) \longrightarrow Hg^*$

(5) $Hg^* + O_2 \longrightarrow 2 O + Hg$
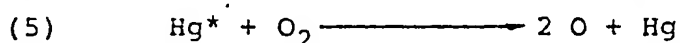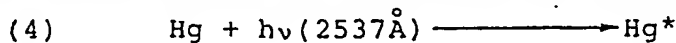
Since molecular oxygen reacts spontaneously with SiH_4

as discussed in relation to the prior art thermal

35   oxidation process, it is necessary to inhibit this

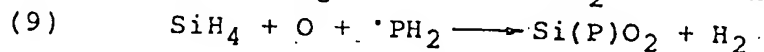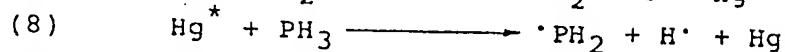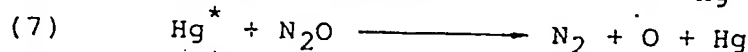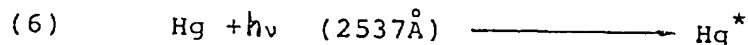spontaneous thermal oxidation process in order to permit

1   the formation of atomic oxygen and the reaction thereof
     with SiH_4 in accordance with the process of the present
     invention. This inhibition is accomplished by carefully
     controlling the operating pressure and the ratio of
5   reactant gases, as discussed in more detail in Example 3
     below. By controlling such process parameters the ther-
     mal oxidation process may be completely inhibited and
     the oxidation process of the present invention may occur
     without any competing processes.
10   By the above-described process of the present
     invention, oxygen atoms are produced by a photochemical
     process which generates only neutral particles. Thus,
     the prior art problems associated with the generation
     of charged particles and high energy radiation which
15   bombard the substrate have been avoided. The value
     of the surface state density (N_{ss}) at the oxide/semi-
     conductor substrate interface and thus the charge
     traps in the oxide or insulator layer are minimized by
     the process of the present invention. In addition, a low
20   density of generation/recombination centers (i.e., dang-
     ling bonds or traps) is produced and thus good minority
     carrier lifetime is achieved in devices formed by the
     process of the present invention. In addition, the
     process of the present invention provides enhanced pro-
25   tection against device damage due to radiation (i.e.
     from a cobalt-60 source) by minimizing the creation of
     dangling bonds and traps during the deposition of the oxide
     or insulator layer. These traps and dangling bonds nor-
     mally increase the probability of radiation damage to
30   the device and their minimization thus reduces the probability of
     radiation damage. Further, the problem of boundary
     migration has been eliminated since the process of the
     present invention can be conducted at a relatively low
     temperature, i.e. as low as room temperature, and the
35   associated problem of decreased device yield encountered
     in the high temperature fabrication of high density

1   devices such as very large scale integrated circuits and
very high speed integrated circuits, has been avoided.
In addition, the prior art problem of plasma-induced
heating is avoided by the process of the present invention
5   since selective absorption of radiation by the substrate
does not occur in the process described herein. Further-
more, the process of the present invention is free of
particulate formation, for example, on chamber walls,
which is a problem often encountered in the prior art
10   processes discussed above. Finally, the oxide layer
formed by the process of the present invention is dense,
non-granular, scratch-resistant, specular, has negligible
porosity, and is strongly adherent to a variety of sur-
faces, such as semiconductor, metal and inorganic sur-
15   faces. Such oxide layers find utility both as a passi-
vation layer and as a gate insulator layer in integrated
circuit devices. Furthermore, these oxide layers may
be used as a conformal coating on integrated circuits
and hybrid microcircuits. In addition, these oxide
20   layers may be used in the fabrication of HgCdTe photo-
conductive and photovoltaic devices. This first process
embodiment of the present invention and the related third
process embodiment discussed below are, to my knowledge,
the first demonstration of the use of a photochemical
25   process for the deposition of a dielectric layer on a
substrate.

    Using the above-described process, the present
invention may also be used to oxidize trimethyl aluminum,
$(CH_3)_3 Al$, to Al_2O_3; trimethyl gallium, $(CH_3)_3Ga$, to
30   Ga_2O_3; germane, GeH_4, to GeO_2; diborane, B_2H_6, to B_2O_3;
trimethyl indium, $(CH_3)_3In$ to In_2O_3; titanium tetra-
chloride, $TiCl_4$, to TiO_2; tungsten hexafluoride, WF_6,
to W_2O_3, and hafnium hydride, HfH_4, to HfO_2. This first
process embodiment of the present invention is illustrated
35   in Example 1 below.

1   Furthermore, a process carried out in accordance
with a second embodiment of the present invention may be
performed by practicing the present invention as described
above, using the apparatus of FIG. 1 with three (3)

5 reactant gas chambers (chambers 26, 27, and 28), to deposit
on the surface of a chosen substrate an oxide layer which
incorporates a selected dopant material in order to
modify the physical, electrical, or optical character-
istics of the oxide layer. To accomplish this second

10 process embodiment of the present invention, the selected
vapor phase reactant, such as SiH_4, is exposed to simul-
taneously formed and photochemically generated neutral
oxygen atoms and neutral atoms or atomic fragments of
the selected dopant, such as phosphorus − containing

15 phosphinyl radicals. The neutral atomic particles are
produced by the mercury photosensitized dissociation
of a chemically unreactive oxygen-containing precursor,
such as nitrous oxide (N_2O) and a chemically unreactive
dopant-containing precursor, such as phosphine (PH_3),

20 which results in the generation of atomic oxygen and
neutral phosphinyl radicals, respectively, as shown
in Equations (6) through (8) below. The atomic oxygen
and phosphinyl radicals subsequently oxidize the SiH_4
to phosphorus-doped silicon dioxide [$Si(P)O_2$], as

25 shown in Equation (9) below.

$$(6) \quad Hg + h\nu \ (2537\overset{\circ}{A}) \longrightarrow Hg^*$$

$$(7) \quad Hg^* + N_2O \longrightarrow N_2 + O + Hg$$

$$(8) \quad Hg^* + PH_3 \longrightarrow {}^{\cdot}PH_2 + H^{\cdot} + Hg$$

$$(9) \quad SiH_4 + O + {}^{\cdot}PH_2 \longrightarrow Si(P)O_2 + H_2$$

30   A mechanistic alternative to the sequence described
above involves the simultaneous oxidation of both SiH_4 and
PH_3 by atomic oxygen, as indicated in Equations (10)
through (12) below. Thus, atomic oxygen alone may be suf-
ficient to bring about the desired reaction as shown in

35 Equation (12) below. Consequently, the production of neu-
tral particles of the selected dopant material as described

1   above in Equation (8) may not be necessary in practicing
the second process embodiment of this invention, but
may occur.

$$(10) \quad Hg + h\nu \ (2537\overset{\circ}{A}) \longrightarrow Hg*$$

5      $$(11) \quad Hg* + N_2O \longrightarrow N_2 + O + Hg$$

$$(12) \quad SiH_4 + PH_3 + O \longrightarrow Si(P)O_2 + H_2$$
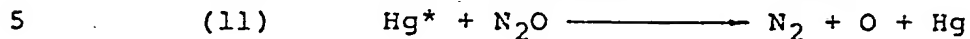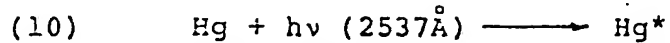
The procedure followed to accomplish this second
process embodiment of the invention is essentially as
described above with respect to the first process embodi-

10   ment of the present invention, except that additionally,
a controlled amount of a selected dopant-containing pre-
cursor is introduced from the chamber 27 through the
control valve 31 into the tube 34, where it mixes with
the reactant gases from the chambers 26 and 28.

15   Thus, by this second process embodiment of the pre-
sent invention, a doped dielectric film may be deposited
by a low-temperature process which avoids the generation
of charged particles and high energy radiation and their
consequent bombardment damage to the substrate. Addition-

20   ally, this embodiment has all the advantages enumerated
above with respect to the formation of an undoped
dielectric layer by the process of the present invention.
This second process embodiment of the present invention
and the related fourth process embodiment discussed below

25   are, to my knowledge, the first demonstration of the
use of a photochemical process for the deposition of
a doped dielectric layer.

By the process according to this second embodiment
of the present invention, other dopants besides phosphorus

30   may be incorporated in the deposited dielectric layer by
addition of the corresponding dopant-containing precursor
to the reactant gas mixture. For example, diborane (B_2H_6)
may be used for boron doping, arsine (AsH_3) may be used for
arsenic doping, stibine (SbH_3) may be used for antimony

35   doping, hydrogen selenide (H_2Se) may be used for selenium
doping, hydrogen sulfide (H_2S) may be used for sulfur

1　doping, or hydrogen telluride (H₂Te) may be used for tellurium doping. Other dopant-containing precursors which are capable of the mercury photosensitized dissociation reaction of the type discussed herein may

5　also be used. Other dielectric films besides SiO_2 may be formed, as discussed above. This second process embodiment of the present invention is illustrated in more detail in Example 2 below.

Turning now to FIG. 2, there is shown an apparatus

10　suitable for implementation of the processes according to of third and fourth embodiments of the present invention, in which neutral oxygen atoms are formed by a direct photochemical reaction of an oxygen-containing precursor, thus eliminating the requirement of mercury photosensitiza-

15　tion. A reaction chamber 40 in which the photochemical vapor deposition reaction occurs is provided with a transparent window 42, which is integral with the top surface of the chamber 40. The material of which the window 42 is formed is chosen to be transparent to the selected

20　wavelength of radiation which will be used for the photochemical reaction. Radiation 44 having a selected wavelength is produced by a radiation-producing means 46, such as an array of low pressure mercury vapor arc lamps, and passes through the window 42 into the chamber

25　40. Within the reaction chamber 40, there is a substrate holder 48, which holds a substrate 50 onto which the desired oxide layer is to be deposited. External to the reaction chamber 40 at the bottom surface thereof, there are heating elements 51, which may be formed of Nichrome

30　wire and are activated by application of a controlled voltage thereto. The heating elements 51 may be used optionally to preheat the substrate 50 to the required temperature for forming a deposited layer with desired properties.
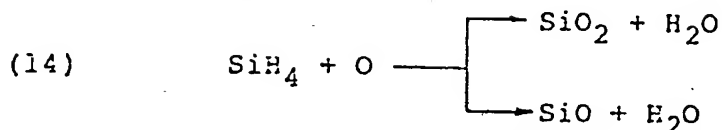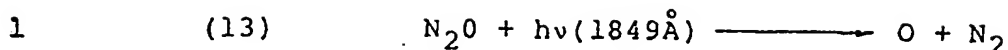
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1　　　　In practicing the present invention, the temperature
in the chamber 40 may be maintained as low as room tempera-
ture or as high as 200°C or higher.　In order to provide
the required cooling of the radiation-producing means 46,
5　as previously discussed in relation to FIG. 1, radiation-
producing means 46 is completely enclosed within the
enclosure 53, which may be formed of aluminum, and an
external cooling means 55, such as pipes with water flow-
ing therethrough as shown in FIG. 2 or flowing nitrogen
10　gas, is activated to apply cooling to the enclosure 53.
The enclosure 53 performs the additional function of
eliminating the formation of ozone which would occur if
the radiation 44 (such as 1849 Å radiation) were allowed
to contact molecular oxygen in the open atmosphere,
15　which would cause the formation of atomic oxygen that
would then react with additional molecular oxygen in
the atmosphere to form ozone.　The enclosure 53 is
secured to the outside surface of the reaction chamber
40 which surrounds the quartz window 42, but may be
20　removed therefrom as required.

　　　　Leading from the reaction chamber 40, there is a
tube 52 which passes through a valve 54 and then to a
vacuum producing means, e.g., a vacuum pump, (not shown)
which is used to evacuate the chamber 40 to a sufficiently
25　low pressure (e.g., 1-4 Torr) to allow the vapor deposition
reaction to occur.

　　　　External to the reaction chamber 40, there are
chambers 56 and 58, which contain the individual selected
reactant gases, such as silane (SiH_4) and nitrous oxide
30　(N_2O), respectively, for producing the desired photo-
chemical reaction.　The chambers 56 and 58 are connected
to control valves or flowmeters 60 and 62, respectively,
which are used to control the amounts of reactants which
are introduced into a tube 64.　Alternatively, in accord-
35　ance with a fourth process embodiment of the present
invention (discussed below), there are included a third

1   chamber 57, which contains the precursor of the selected
dopant material, such as phosphine, and a corresponding
control valve or flowmeter 61, which controls the amount
of dopant precursor introduced from the chamber 57 into
5   the tube 64, where it is mixed with the other reactant
gases discussed above. The reactant gases flow through
the tube 64 into the reaction chamber 40, where the
photochemical reaction may be brought about. The compo-
nents of the apparatus shown in FIG. 2 may be constructed
10   of stainless steel or aluminum, unless otherwise speci-
fied. The apparatus shown in FIG. 2 may be used for
either a continuous flow photochemical reactor system
or a static photochemical reactor system, as discussed
above with reference to FIG. 1.
15   In practicing the present invention in accordance
with the third embodiment thereof and using the apparatus
of FIG. 2, the general process described in relation
to the first process embodiment of FIG. 1 is followed,
except that no mercury is used for photosensitization.
20   The valves 60 and 62 are set so that the reactant gases,
such as SiH_4 and N_2O, from the chambers 56 and 58,
respectively, pass in a predetermined ratio and at a
predetermined flow rate into the tube 64 and then into
the reaction chamber 40. The radiation-producing means 46
25   is activated and produces the radiation 44 of a selected
wavelength, which is the appropriate wavelength to cause
the direct dissociation of the selected oxygen-containing
precursor (e.g. 1750-1950Å for N_2O). The radiation 44
passes through the window 42, which is formed of a mate-
30   rial that is transparent to the wavelength of the radia-
tion 44. The radiation 44 passes into the reaction cham-
ber 40, where it causes the dissociation of the selected
oxygen-containing precursor, such as N_2O, into atomic
oxygen, which then reacts with the selected vapor phase
35   reactant, such as SiH_4, to form the desired oxide, such as
SiO_2 and SiO, as shown in Equations (13) and (14) below.

1

(13) $N_2O + h\nu(1849\text{Å}) \longrightarrow O + N_2$

(14) $SiH_4 + O \longrightarrow \begin{cases} SiO_2 + H_2O \\ SiO + H_2O \end{cases}$

5   Alternatively, the atomic oxygen required for this third process embodiment of the present invention may be formed by the direct photochemical dissociation of molecular oxygen as shown in Equation (15) below or of nitrogen dioxide (NO_2) as shown in Equation (16) below

10 or of similar known materials which are capable of dissociation to oxygen by a direct photochemical process.

(15) $O_2 + h\nu(1849\text{Å}) \longrightarrow 2\ O$

(16) $NO_2 + h\nu(3500\text{-}6000\text{Å}) \longrightarrow O + NO$
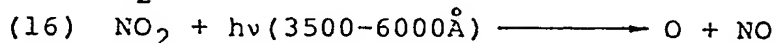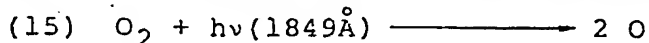
When molecular oxygen is used as the source of atomic

15 oxygen, the operating pressure and reactant gas ratio must be carefully controlled in order to inhibit the spontaneous thermal oxidation of the SiH_4 by the O_2, as previously discussed in relation to an alternative process embodiment of the present invention and as

20 illustrated in Example 3 below.

      By the above-described process in accordance with this third embodiment of the present invention, oxygen atoms are generated by a photochemical process which produces only neutral particles. Thus, the previously

25 discussed prior art problems caused by the generation of charged particles and high energy radiation and their bombardment of the substrate have been avoided. The advantages of this third process embodiment of the present invention are the same as those discussed in relation

30 to the first process embodiment described with respect to FIG. 1. In addition, the process according to this third embodiment has the advantage that no photosensitizing mercury is necessary, and thus possible mercury contamination of the deposited oxide can be avoided. Further,

35 the apparatus for carrying out the process according

1   to this third embodiment is less complex than an apparatus
   requiring the use of mercury.

         Using the above-described process, the present
     invention may also be used to deposit dielectric oxides
5   of gallium, germanium, boron, and indium and metal oxides
     of aluminum, tungsten, titanium, and hafnium, using the
     gas phase reactants discussed in relation to FIG. 1.
     This third process embodiment of the present invention
     is illustrated in Example 3 below.

10   Furthermore, a process carried out in accordance
     with a fourth embodiment of the present invention may
     be performed by practicing the present invention as
     described above, but also using the apparatus of FIG. 2
     with three (3) reactant gas chambers (chambers 56, 57,
15   and 58), to deposit an oxide layer which incorporates
     a selected dopant material, on the surface of a chosen
     substrate. To accomplish this fourth process embodi-
     ment of the present invention, the selected vapor phase
     reactant, such as SiH_4, is exposed to photochemically
20   generated neutral oxygen atoms in the presence of a
     dopant-containing precursor, such as phosphine (PH_3).
     The neutral atomic oxygen is produced by direct dissocia-
     tion of an oxygen-containing precursor, such as N_2O,
     by radiation of a selected wavelength as shown in Equa-
25   tion (17) below. The atomic oxygen then simultaneously
     oxidizes the SiH_4 and PH_3 to form the desired phosphorus-
     doped SiO_2 as shown in Equation (18) below.

     (17) $N_2O + h\nu(1849\overset{\circ}{A}) \longrightarrow O + N_2$
     (18) $SiH_4 + PH_3 + O \longrightarrow Si(P)O_2 + H_2$
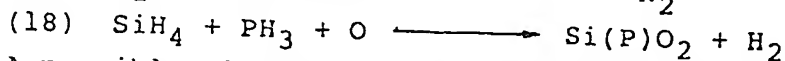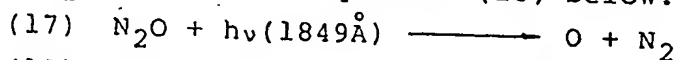
30   A possible alternative to the above-described
     sequence involves the direct dissociation of the dopant-
     containing precursor such as phosphine to form a neutral
     phosphinyl radical as shown in Equation (19) below. The
     phosphinyl radical so formed and the atomic oxygen formed
35   in accordance with the direct dissociation reaction of
     Equation (17) above then react with the silane reactant

1 to form the desired phosphorus-doped SiO_2 as shown in
Equation (20) below.

(19) $PH_3 + h\nu(1849\mathring{A}) \longrightarrow \cdot PH_2 + H\cdot$

(20) $SiH_4 + O + \cdot PH_2 \longrightarrow Si(P)O_2 + H_2$
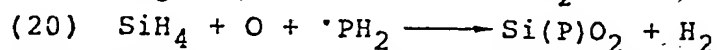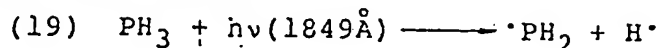
5 The procedure followed to accomplish the process
according to the fourth embodiment of this invention
is essentially as described above with respect to the
third process embodiment of the present invention, except
that additionally a controlled amount of a selected
10 dopant-containing precursor, such as phosphine gas, is
introduced from the chamber 57 and through the valve 61
into the tube 64, where it mixes with the reactant gases
from the chambers 56 and 58.

Thus, by this fourth process embodiment of the
15 present invention, a doped dielectric film may be
deposited by a low-temperature process which avoids
the generation of charged particles and high energy radia-
tion and their consequent bombardment damage to the
substrate and additionally avoids the use of mercury
20 for photosensitization. The significance of these
advantages has been discussed above with respect to
the third process embodiment of the present invention.
Various dopant materials other than phosphine may be
used, and these materials include diborane, arsine,
25 stibine, hydrogen selenide, hydrogen sulfide, hydrogen
telluride, or other dopant-containing precursors which
are capable of simultaneous oxidation by atomic oxygen
with the selected gas phase reactant to form the desired
doped oxide layer. This fourth process embodiment of
30 the present invention is illustrated in Example 4 below.

EXAMPLE 1

This example illustrates the use of the process
according to the first embodiment of the present inven-
35 tion as previously described herein.

1   Using the apparatus described and illustrated in
relation to FIG. 1 with two reactant gas chambers, SiO
and SiO_2 were independently deposited on the surface
of a wafer of silicon having a two-inch diameter. Nitrous
5   oxide was used as the oxygen-containing precursor and
silane was the selected vapor phase reactant. The reac-
tion chamber 10 was evacuated by the vacuum-producing
means to a pressure of 10^{-3} Torr, then back-filled with
nitrogen, and again evacuated to a pressure of 10^{-3} Torr.
10   The flowmeters 30 and 32 were activated to admit the
reactant gases (SiH_4 and N_2O) in a predetermined ratio
into the tube 34 and subsequently into the chamber 36
and the reaction chamber 10, and the reactant gas flow
rates were stabilized. The operating pressure within the
15   reaction chamber 10 was adjusted by means of the valve 24
to achieve a pressure of approximately 1 Torr. The heat-
ing elements 21 and the cooling means 25 were activated.
Finally, the low pressure mercury arc resonance lamps
were activated and emitted radiation at 2537Å, which
20   was absorbed by the mercury vapor in the reaction
chamber, producing photo-excited mercury atoms, which
collided with the nitrous oxide to form atomic oxygen.
The atomic oxygen then oxidized the silane to either
SiO_2 or SiO. When using a continuous flow photochemical
25   reactor system at an operating pressure of 2 Torr, with
a reactant gas flow ratio of 2 standard cubic centimeters
per minute (sccm) of SiH_4 to 50 sccm of N_2O, a layer of
SiO_2 was produced. When a reactant gas flow ratio of
2 sccm of SiH_4 to 10 sccm of N_2O was used in a continuous
30   flow system, a layer of SiO was produced. At a substrate
temperature of 100°C, the silicon oxide layer was deposi-
ted at the rate of 200Å per minute using a continuous
flow system. When using a static photochemical reactor
system with a reactant gas ratio of SiH_4 to N_2O of 3
35   millimeters (mm) to 12 mm, silicon monoxide (SiO) was
produced as a layer on the surface of the silicon wafer.

1   When a reactant gas ratio of SiH_4 to N_2O of 3.0mm to 30mm
     was used in a static system, silicon dioxide (SiO_2)
     was produced as the layer on the silicon wafer.
          The refractive index of the photodeposited silicon
5   oxide layers formed by the process of this embodiment of
     the present invention was determined by ellipsometry
     as a function of the reactant gas mixture ratio, N_2O/SiH_4.
     Mixtures rich in N_2O (i.e. atomic oxygen) produced
     films with a refractive index characteristic of SiO_2,
10   i.e. 1.45. Mixtures of N_2O/SiH_4 progressively leaner
     in N_2O yielded silicon oxide films with less oxygen
     content and, ultimately, SiO with a refractive index
     of 1.88. The etch rate characteristics of the photo-
     deposited SiO_2 material in buffered HF were comparable
15   to those of SiO_2 films deposited by low temperature plasma
     techniques. The stoichiometric composition of the film
     was determined by Auger electron spectroscopy. The SiO_2
     films exhibited an excellent composition/depth pro-
     file and stoichiometrically were equivalent to pure
20   SiO_2. The SiO films exhibited slower etch rates than
     the SiO_2 films due to the depleted oxygen content of
     the SiO films, which was confirmed by Auger spectroscopic
     analysis. The breakdown voltage of the SiO_2 films formed
     by the process of the present invention was determined
25   to be 3.0×10^6 volts/centimeter, the dielectric constant
     was approximately 5.5, and the dissipation factor was
     1.5×10^{-2}, which measurements are comparable to the
     values obtained for similar films formed by a prior art
     thermal process previously discussed. The density of
30   the SiO_2 films formed by the process of the present
     invention was 2.3 grams/cubic centimeter.
          The photochemically deposited SiO_2 layers formed
     by the above-described process of the present invention
     have application as dielectric layers for the passivation
35   of semiconductor devices, particularly charge-sensitive
     microelectronic devices, such as silicon MOS devices,

1 HgCdTe photoconductive and photovoltaic devices, and GaAs field-effect transistors. These layers may be deposited to a typical thickness of 1200-1500Å for such a purpose. In addition, the process of the present inven-

5 tion may be used to deposit an anti-reflective oxide coating on a lens, including a plastic lens, or a solar cell, or to deposit a protective oxide coating on a mirror.

Using the above-described process, SiO_2 layers were similarly deposited on Ge, InSb, and Al substrates.

10

EXAMPLE 2

This example illustrates the use of the process according to the second embodiment of the present invention as previously described herein.

15 Using the apparatus described and illustrated in relation to FIG. 1 with three reactant gas chambers, a layer of phosphorus-doped SiO_2 was deposited on the surface of a silicon wafer having a two-inch diameter. The general procedure described in relation to Example 1

20 above was followed, with the addition of a third reactant gas. Nitrous oxide was used as the oxygen-containing precursor, silane was the selected vapor phase reactant, and phosphine was the phosphorus dopant-containing pre- cursor. The process was initiated by the photochemical

25 excitation of mercury vapor at 10^{-3} Torr in a quartz reaction chamber. Low pressure mercury arc resonance lamps emitted radiation at 2537Å, which was absorbed by the mercury vapor in the reaction chamber, producing photo-excited mercury atoms that reacted with the N_2O

30 and PH_3 as shown in Equations (7) and (8) discussed above. The atomic oxygen and neutral phosphinyl radical ($\cdot PH_2$) thus formed reacted with the SiH_4 to form phosphorus- doped silicon dioxide $[Si(P)O_2]$ as shown in Equation (9) discussed above, which deposited as a layer on the

35 silicon wafer. Using a continuous flow photochemical reactor system, with a reactant gas flow ratio of

1    $SiH_4/N_2O/PH_3$ of 2/60/1 sccm, a phosphorus-doped SiO_2 layer was deposited on the substrate at the rate of 200Å/minute and the phosphorus content of the deposited layer was approximately 5%. In addition, a low pressure

5   static photochemical reactor system was used with a reactant gas ratio of $SiH_4/N_2O/PH_3$ of 3/30/1 mm. The phosphorus-doped SiO_2 layer was deposited at initial rates of 200Å/minute and the phosphorus-content in the deposited layer was approximately 5%. Using a reactant

10   gas ratio of $SiH_4/N_2O/PH_3$ of 2/30/12 mm in a static system, levels of phosphorus-doping of 17% in the deposited layer have been achieved.

The refractive index of the photodeposited phosphorus-doped SiO_2 layer was dependent on the N_2O/PH_3

15   ratio and indices from 1.55 to 1.65 were measured. The films exhibiting the higher refractive indices indicated a greater phosphorus doping content of the SiO_2 dielectric material. The chemical composition of the phosphorus-doped SiO_2 films was determined by Auger electron spectro-

20   scopy and the phosphorus content was confirmed by energy dispensive X-ray analysis (EDAX). The etch rate in "P-etch" [i.e., a mixture of 60 milliliters (ml) of water, 3 ml of 49% HF, and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2 films was significantly faster than that of

25   pure SiO_2, yielding values of 200Å/second, which concur with values of phosporus-doped films produced by known chemical vapor deposition techniques previously dis-cussed. The amount of dopant contained in the dielectric layer deposited by the above-described process may be

30   controlled by adjusting the amount of dopant-containing precursor which is added to the reactant gas mixture.

Although phosphorus-doped SiO_2 layers were formed as described above, it is also possible to form .phosphorus-doped SiO layers by this process embodiment

35   of the present invention by increasing the ratio of SiH_4 to N_2O in a manner similar to that described in Example 1.

1   The photochemically deposited phosphorus-doped
SiO_2 films formed by the above-described process of the
present invention have application as dielectric layers
for the passivation of charge-sensitive microelectronic
5   devices, such as silicon MOS devices. In addition, these
phosphorus-doped films may be used as a counter-diffusion
layer on GaAs devices for the minimization of out-
diffusion of both gallium (Ga) and arsenic (As) at tempera-
tures exceeding 100°C.
10

EXAMPLE 3

This example illustrates the use of the process
in accordance with the third embodiment of the present
invention as previously described herein.

15   Using the apparatus shown in FIG. 2 with two
reactant gas chambers, a layer of SiO_2 was deposited on
the surface of a wafer of silicon having a two-inch
diameter. The general procedure described in relation
to Example 1 above was followed, except that mercury

20   sensitization was not used. A continuous flow photo-
chemical reactor system was used. The oxygen-containing
precursor was N_2O and the selected vapor phase reactant
was SiH_4. Radiation having a wavelength of 1849Å
was used to dissociate the N_2O; and the window of the

25   reaction chamber was formed of "spectrasil" (obtained
from Thermal American Fused Quartz, Montville, New
Jersey), which was transparent to 1849Å radiation. Low
pressure mercury arc lamps designed with "spectrasil" en-
velopes emitted radiation at 1849Å, which was transmitted

30   through the "spectrasil" window into the reaction chamber.
The radiation was absorbed by the N_2O and caused dissocia-
tion thereof to produce atomic oxygen. The atomic oxygen
then reacted with the SiH_4 to produce the desired SiO_2
which deposited as a layer on the silicon wafer. A

35   reactant gas flow ratio of SiH_4 to N_2O of 2 sccm to 60
sccm and an operating pressure of 3.7 Torr were used. The

1   SiO_2 layer was deposited at the rate of 700Å in 30 min-
utes, and even higher rates may be achieved with process
optimization.

The refractive index of the photodeposited SiO_2
5   layer formed by the above-described process of the
present invention was determined by ellipsometry and
the films were found to have a refractive index char-
acteristic of SiO_2, i.e. 1.45. The etch rate char-
acteristics of the photodeposited SiO_2 material in
10   buffered HF were comparable to those of SiO_2 films
deposited by low temperature plasma techniques.

Although SiO_2 layers were formed as described
above, it is also possible to form SiO layers by this
process embodiment of the present invention by increasing
15   the ratio of SiH_4 to N_2O in a manner similar to that
described in Example 1.

The photochemically deposited SiO_2 layers formed
by the above-described process of the present invention
have application as dielectric layers for the passivation
20   of semiconductor devices, particularly charge sensitive
microelectronic devices, such as MOS devices and GaAs,
HgCdTe photoconductive and photovoltaic devices, field-
effect transistors. In addition, the oxide layers formed
by the above-described process may be used on electro-
25   optical materials such as lenses and mirrors or on solar
cells as described in relation to Example 1.

Using the above-described process, SiO_2 layers
were similarly deposited on Ge, InSb, and Al substrates.

Furthermore, using the general process described
30   above, a layer of SiO_2 was deposited on the surface of
a silicon wafer, using molecular oxygen (O_2) as the
oxygen-containing precursor. In order to completely in-
hibit the spontaneous thermal oxidation reaction of O_2
and SiH_4, a nitrogen gas diluent was used and the pressure
35   and flow rate conditions of the reactant gases were care-
fully controlled. Using an operating pressure of 0-5 Torr

1   and a reactant gas flow ratio of $SiH_4/O_2/N_2$ of 1/20/80

sccm, a layer of SiO_2 was deposited at the rate of 3000

to 4000Å in 30 minutes. Thus, it may be seen that the

use of molecular oxygen as the oxygen-containing precursor

5   in practicing the present invention greatly enhances the

oxide deposition rate.

EXAMPLE 4

    This example illustrates the use of the process

10   in accordance with the fourth embodiment of the present

invention as previously described herein.

    Using the apparatus described and illustrated in

relation to FIG. 2 with three reactant gas chambers, a

phosphorus-doped SiO_2 layer was deposited on the surface

15   of a silicon wafer having a two-inch diameter. The gene-

ral procedure described in relation to Example 3 above

was followed, with the addition of a third reactant gas.

A continuous flow photochemical reactor system was used.

Nitrous oxide was used as the oxygen-containing precursor,

20   silane was the selected vapor phase reactant, and phos-

phine was the dopant-containing precursor. Radiation

having a wavelength of 1849Å was used to dissociate

the N_2O and the window of the reaction chamber was formed

of "spectrasil" as discussed in relation to Example 3.

25   The 1849Å radiation was absorbed by the N_2O and caused

dissociation thereof to produce atomic oxygen. The atomic

oxygen then reacted with the SiH_4 and PH_3 as shown in

Equation (18) above, to produce the desired phosphorus-

doped SiO_2, which deposited as a layer on the silicon

30   wafer. A low pressure continuous flow photochemical

reactor system was used with a reactant gas flow ratio of

$SiH_4/N_2O/PH_3$ of 2/60/4 sccm. The SiO_2 was deposited at

the rate of 330Å in 30 minutes, and even higher rates may

be achieved with process optimization. The phosphorus-

35   content of the deposited layer was approximately 5%.

1   The refractive index of the photodeposited phos-
phorus-doped SiO_2 layer formed as described above was
1.75. The chemical composition of the deposited film
was determined by Auger electron spectroscopy to be
5   the value discussed above. The etch rate in "P-etch"
[i.e., a mixture of 60 ml of water, 30 ml of 49% HF,
and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2
film was determined to be significantly faster than that
of pure SiO_2, having values comparable to phosphorus-
10   doped films produced by known chemical vapor deposition
techniques previously discussed.

The photochemically deposited phosphorus-doped
SiO_2 films formed by the above-described process of the
present invention find utility as discussed in relation
15   to Example 2.

While the present invention has been particularly
described with the respect to the preferred embodiments
thereof, it will recognized by those skilled in the art
that certain modifications in form and detail may be
20   made without departing from the spirit and scope of the
invention. In particular, the scope of the invention
is not limited to the photochemical vapor deposition
of silicon oxides, but is intended to include the
photochemical vapor deposition of an oxide of any gas
25   phase reactant that will react with atomic oxygen, such
as reactants containing germanium, gallium, boron, indium,
aluminum, titanium, tungsten and hafnium. In addition,
the chemically unreactive oxygen-containing precursor is
not limited to nitrous oxide, molecular oxygen, or nitrogen
30   dioxide, but is intended to include any material which
will photochemically dissociate to atomic oxygen, either
with or without mercury sensitization. Further, the
substrate on which oxide deposition may be performed by
the process of the present invention is not limited to
35   silicon, which was used merely as an example, but may
include other semiconductor substrate materials, such as

1   GaAs, HgCdTe, or InSb, or electro-optical materials, such
    as lenses or mirrors, or GaAs or Si solar cells. Finally,
    the scope of the invention is not limited to the use of
    phosphine to produce phosphorus-doping, but is intended
5   to include any dopant-containing precursor which is
    capable of mercury photosensitized dissociation to form
    neutral particles or which is capable of simultaneous
    oxidation by atomic oxygen with the selected gas reactant.
    Such precursors include diborane, arsine, stibine, hydrogen
10 selenide, hydrogen sulfide, or hydrogen telluride, to
    produce boron-, arsenic-, antimony-, selenium-, sulfur-,
    or tellurium-doping, respectively.

15

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BAD ORIGINAL

CLAIMS

1. A process for forming a layer of an oxide of a chosen material on the surface of a selected substrate, comprising the steps of exposing the substrate to a vapor-phase reactant and an oxygen-containing precursor in the presence of radiation of a predetermined wavelength to photochemically generate neutral oxygen atoms which react with the vapor-phase reactant to form said oxide layer under selected temperature, pressure and flow rate conditions.

2. A process according to claim 1, wherein said vapor-phase reactant contains silicon, germanium, gallium, boron, indium, aluminum, titanium, tungsten, or hafnium.

3. A process according to claim 2, wherein said vapor-phase reactant is silane (SiH_4) and said oxide is silicon dioxide and/or silicon monoxide.

4. A process according to any preceding claim, wherein said oxygen-containing precursor is nitrous oxide (N_2O), nitrogen dioxide (NO_2), or molecular oxygen (O_2).

5. A process according to any preceding claim, wherein the oxide layer is formed in the presence of photochemically generated dopant atoms to incorporate the dopant atoms into said oxide.

6. A process according to any preceding claim, wherein mercury vapor is added to said reactant and said precursor to cause mercury photosensitized dissociation of a chosen oxygen-containing precursor.

7. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a static photochemical reactor whereby the gas ratio of SiH_4 to N_2O is 3 to 12 millimeters, and the temperature at which the process is maintained is 30 to $200^{\circ}C$.

8.   A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a continuous flow photochemical reactor whereby the gas flow ratio of SiH_4 to N_2O is 2 to 10 standard cubic centimeters per minute (sccm), and the temperature at which the process is maintained is 30 to 200°C.

9.   A process according to any of the claims 1-5, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the predetermined wavelength is 1750 to 1950Å, the gas flow ratio of SiH_4 to N_2O is 2 to 60 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon dioxide (SiO_2).

10.   A process according to any of the claims 1-5, wherein the oxygen-containing precursor is molecular oxygen (O_2) and nitrogen (N_2) is admixed thereto, said predetermined wavelength is 1849Å, the vapor-phase reactant is silane (SiH_4), said pressure is 0 to 5 Torr, and the gas flow ratio of SiH_4 to O_2 to N_2 is 1 to 20 to 80 standard cubic centimeters per minute.

11.   A process according to claim 5 or 6, wherein there is provided a dopant-containing precursor which is phosphine (PH_3), diborane (B_2H_6), arsine (AsH_3), stibine (SbH_3), hydrogen selenide (H_2Se), hydrogen sulfide (H_2S), or hydrogen telluride (H_2Te).

JS:ad

Fig. 1

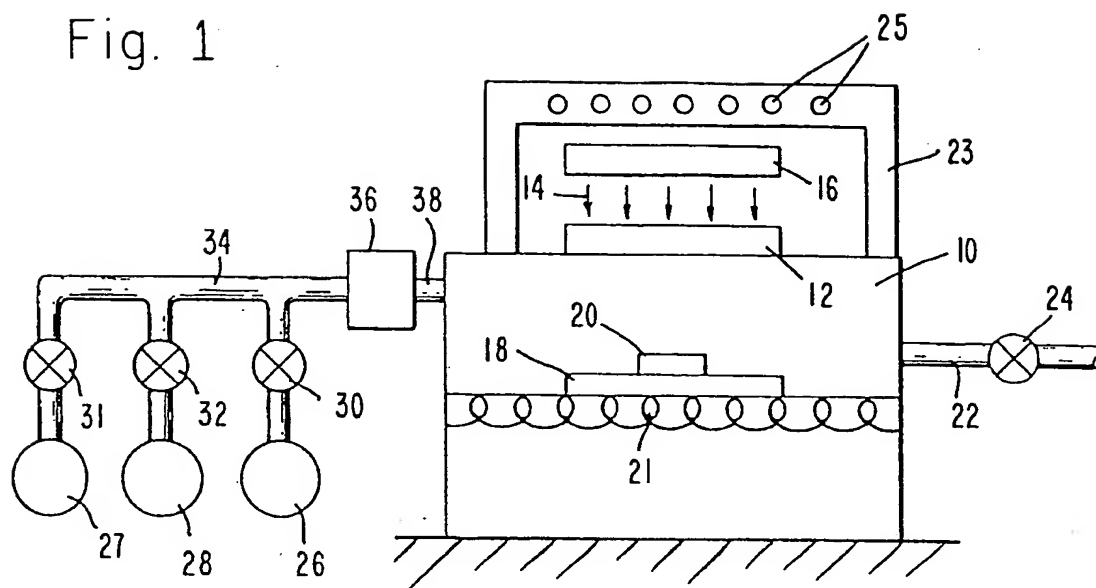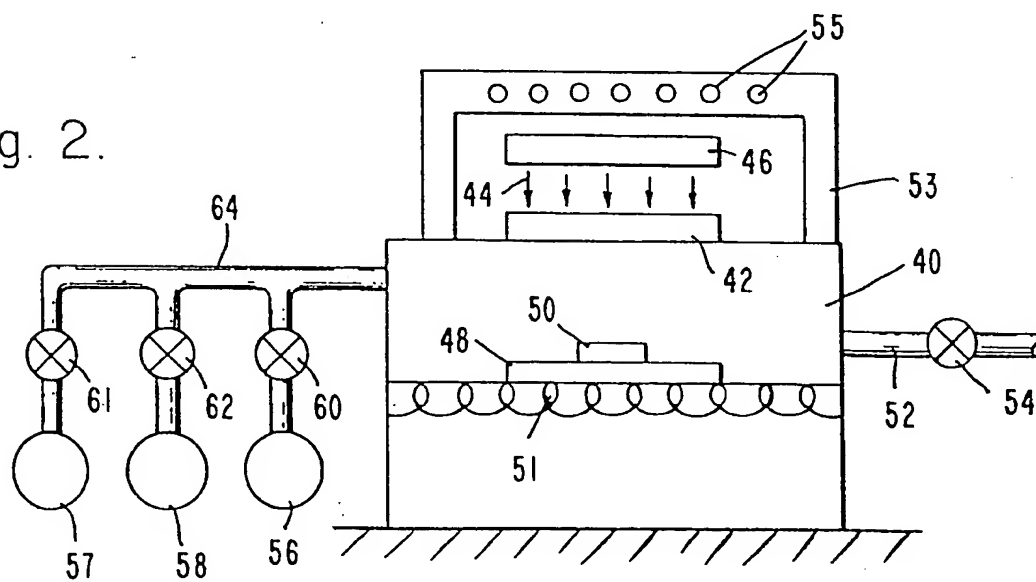Fig. 2.

EUROPEAN SEARCH REPORT

European Patent Office

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	<u>DE - A - 1 564 963</u> (TEXAS) + Totality + --	
	<u>AT - B - 287 789</u> (N.V. PHILIPS) + Totality; especially claims 1,2,4,6 + --	
A	<u>DE - B - 1 444 520</u> (RCA) + Totality; especially column 2, line 63 - column 4, line 8; claims 1,2 + --	
A	<u>US - A - 3 767 484</u> (TAKAGI) + Totality; especially column 3, line 68 - column 4, line 3 + --	
A	<u>US - A - 3 907 616</u> (WIEMER) + Totality; especially column 6, line 49 - column 7, line 10; claims 1,5,7,8 + --	
	<u>US - A - 3 769 104</u> (ONO) + Totality; especially column 2, line 67 - column 3, line 21 + --	
D,A	JOURNAL OF VACUUM SCIENCE & TECHNOLOGIE, Vol. 14, No. 5, Sept./Oct. 1977 KERN-ROSIER "Advances in deposition process for passivation films", pages 1082-1099 + Totality + --	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

H 01 L 21/205
H 01 L 21/225
H 01 L 21/268//
H 01 L 21/316
H 01 L 21/365
H 01 L 21/385
H 01 L 21/428

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

B 41 N
G 03 F
H 01 L

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X	The present search report has been drawn up for all claims		
Place of search VIENNA	Date of completion of the search 19-02-1981	Examiner FRANZ	

EPO Form 1503.1 06.78

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,A	JOURNAL OF VACUUM SCIENCE & TECHNOLOGIE, Vol 14, No. 5, Sept./Oct. 1977 AMICK-SCHNABLE-VOSSEN "Deposition techniques for dielectric films on semiconductor devices", pages 1053-1063 + Totality +		

DOCUMENTS CONSIDERED TO BE RELEVANT

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)